Pathways of transfer of Pb, Cd and Zn in highly contaminated soils

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Abstract

Our multidisciplinary research dealt with the ways and mechanisms of transfer of pollutants from one industrial site to the top soil and within the soil to the water table. The zone of study is an area wider than 100 km^2 surrounding two industrial places located in the Nord-Pas de Calais, North of France. Soils of the area are contaminated as a result of close to 100 years of industrial release of dust particles with high Pb, Cd and Zn contents. In the top soil, Pb contents are higher than 1000 mg kg^{-1} up to 1000 m from the source, where wind influence is maximum.

Different models of air transportation have been tested, taking into account the particle sizes in the smoke and wind characteristics (speed and direction). The question is how to improve model accuracy and separate the effects of the smoke stacks from those of the dust coming from the working surface of the industrial sites or from the neighbouring highway. The measurement of the physico-chemical characteristics of different soil profiles shows that, if most of the contamination is to be found in the topsoil, traces of Cd and Zn can accumulate until a depth of 2 m. Moreover, the metals could have migrated beyond the horizons where they were detected. The depth reached by the contamination first depends on the metal concentration in the topsoil. Earthworm galleries act also as paths wherein metals migrate downwards.

Lysimetric sets allow one to follow the quality of soil solution at different depth in relatively undisturbed soils. The role of the organic or mineral colloids as metals carriers appears to be important in the case of lead transfer and has to be taken into account as well as the water soluble fraction.

In a different way, the porosity of the soil is also an important characteristic of the pollutant transfer capability. Thin sections were used to characterise and measure this porosity in relation with observed deposit places and detailed metals position.

The results from first stage support the need to have a multidisciplinary approach in understanding pollutant transfer in soils. Chemical and physical investigations at both microscopic to macroscopic scales are required.

Keywords: heavy metal, contaminated soil, lixiviation, porosity

Introduction

In the Nord-Pas de Calais Region (north of France) are located two of the most important lead and zinc production sites in Europe (Figure 1). They have both more than one century of activity and are less than 5 km of flat terrain distant. The atmospheric metal emissions generated by these smelters have resulted in the contamination of the surrounding soils by cadmium, lead and zinc (Luttringer & de Cormis, 1979).

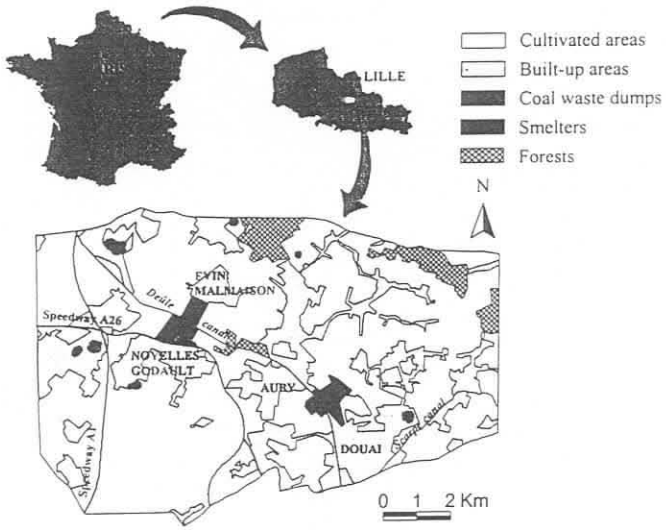

Figure 1. Location map.

Given this soil contamination in relatively important population and agricultural area, led the Nord-Pas de Calais Regional Council to initiate and support a specific multidisciplinary research programme called "Programme de Recherches Concertées". Around such a multidisciplinary programme several working groups dealing with speciation of pollutants, their transfer in living organisms, including crops and man, economical and sociological effects of the pollution were identified. Each working group had its own speciality but all of them working on the same object and final objective.

Despite the fact that this contamination has long been known, few studies have been carried out into its vertical distribution in the soils. So, one of groups aims was the question of the dissemination of the metallic pollutants, including their transfer from the stacks to the soil and then their vertical migration within cultivated or non-cultivated soils. In the first stage, different teams had different approaches according to different points of view. The purpose of this paper is to try to compare the results of the different approaches and how this aid in understanding of the rules of transfer of metallic pollutants within the soils.

Aerial dispersion from industrial plants

For this research, we used a dispersion model to simulate the dust transport arising from the two metallurgical units. In this first approach, we neglected the diffusive sources, and considered only the stacks sources from the two plants.

In order to calibrate the model, a measuring campaign was established around the industrial plants. Initial emissions were measured from the main stack of the plants, driven with the normalised protocol NFX 44052. Using filter for sampling, the dust taken into account have a maximum diameter of 20 µm. We obtained measurements of the mass of Cd, Pb and Zn emitted in the main stack of the plants.

The sampling of dust around the two industrial sites were made using the normalised protocol NFX 43007 with deposition plates. Eighteen sampling points were situated on circles from 1000 m to 2500 m around the two plants. The deposition plates were exposed weekly during twelve weeks, and the dust stuck on the filters with the aid of silicon fat. After extraction and solubilisation, concentrations of Cd, Pb and Zn were measured. The granulometry of the dust has been determined on the same samples. The weather conditions are known from a meteorological mast situated in one of the two plants (hourly wind speed and direction) and from data of Météo France.

Results

We used the ISC gaussian model (Industrial Source Complex) from l'US EPA (1987) to simulate the transport of the dust. We made hourly simulation and used the Briggs values of $=_y$ and $=_z$ derived from Pasquill-Gifford stability categories. We assumed plume rise from Briggs (1969) and the reflective coefficients from Mc Mahon (1978). The evaluation of the results was made on the analysis of the Fractional Bias (FB), the Normalized Mean Square Error (NMSE) and the correlation coefficient (COR) recommended by Cox & Tikvart (1990) and Hanna (1988):

$$FB \text{ (Fractional Bias)} = (Com - Ccm) / (0{,}5(Com + Ccm)), \quad (1)$$

$$NMSE \text{ (Normalized Mean Square Error)} = (Com - Ccm) / (Com.Ccm), \quad (2)$$

$$COR\text{(Correlation)} = (Co - Com)(Cc - Ccm) / (sigO.sigC) \quad (3)$$

with Co, Com, sigO and Cc, Ccm, sigC respectively concentration, mean concentration and standard deviation of the observed and calculated concentrations.

The results obtained were : FB = -0.12, NMSE = 0.65, COR = 0.77.

The calculated results show a good agreement with the measurements. This validation permitted to calculate the maps of yearly ground depositions. We used statistical weather data to build the maps of Cd, Pb, and Zn annual deposition (Figure 2).

Discussion

We applied a gaussian plume model to simulate the transport of small particles emitted from metallurgical plants. The model shows a good agreement with measures for Cd as well for Pb and Zn distribution. However, in order to improve the quality of the modelling results, we need to perform better evaluation of the emissions and introduce diffusive emissions in the model. In other respects, we observed that the pollutant level in soils of garden, generally

surrounded by hedges, is higher than in the bordering fields (up to 2 or 3 times more). So we have to consider that, if the soil surface is not totally flat, the spread out from dust emitted by the stacks may then have different ways to accumulate on the soil.

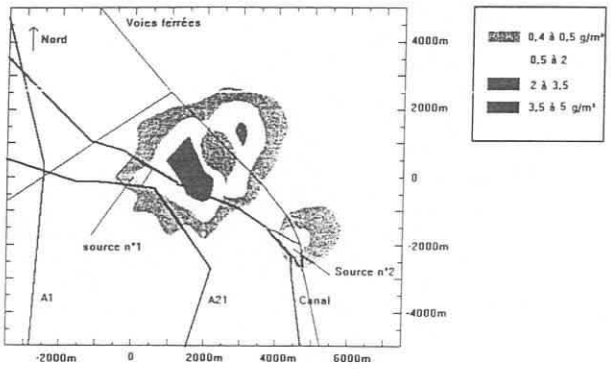

Figure 2 : Cartography of annual zinc ground deposition.

Vertical migration of heavy metals within soils

Vertical distribution

A detailed investigation was done (Sterckeman *et al.*, 1999) in order to evaluate the vertical distribution and the downward mobility of Cd, Zn and Pb in soils around these smelters. Further, it was done in order to determine the factors influencing mobility, and also to test a pedological approach proposed by Baize (1994).

Soils sampling and analyses

The soil cartography of the area determined the choice of profile sites for the study. Two soil units were considered on the basis of their lithological origins : soils developed out of loessic material (Agrudalf) and alluvial soils (Epiaquoll). These soils are referred to as M and UM respectively.

In the contaminated area, six profiles were selected for each soil unit according to their degree of surface contamination and factors like pH, CEC or the organic carbon level. They have been described and sampled down to a depth of 1.5 to 2 m Two control profiles considered as non-contaminated were also sampled outside the area. Furthermore, samples were taken from the material obstructing the earthworm galleries observed in some profiles. These conduits were partially filled with deposits of a darker colour than that of the horizon at the same depth. Samples were then air dried, crushed and passed through a 2 mm sieve. A representative subsample was ground to 0.315 mm for total dissolution.

Besides the classical basic analyses, Cd, Pb and Zn total concentrations were determined according to Ciesielski *et al.* (1997) and NF X 31-147 standard.

Results and discussion

Identification of depth reached by the migration of trace elements in soil requires the knowledge of the original contents of these elements in soil (i.e. pedo-geochemical background content). These background values are estimated both by comparison with non contaminated soils and correlations which were found between the levels of the trace element under consideration (Cd, Pb or Zn) and pedological parameters non modified by contamination (total Al gives the best results in our situation, secondly clay or sand contents). The background value fluctuate for the most part between 10 and 20 mg kg^{-1} for Pb, between 40 and 60 mg kg^{-1} for Zn and between 0.1 and 0.2 mg kg^{-1} (or even less for the sandiest horizons) for Cd. The analysis of the soil profiles shows that the greater contamination is found in the upper 20 to 30 cm, the concentrations of Cd, Pb or Zn decrease abruptly downward, but that the contaminants can migrate to relatively great depth.

A Pb enrichment is suspected to depths of 1.2 m for M8, 0.6 m for M6, 0.5 m for UM4, no lower than 0.4 m in UM9 (Table 1). A Zn enrichment can be diagnosed as deep as 0.8 m for M8, 0.6 m for M6, 0.4 m for UM9 and about 1.2 m for UM4. For Cd, it appears that soils M8 and UM4 are contaminated up to a depth of around 1.2 m, M6 to 0.6 m, UM9 around 0.4 m.

Complementary observations or comments can be done:

(1) The Zn profile of UM1 differs from the others (Table 1). The Zn/clay relationship reveals the contamination of UM17, to approximately 1.3 m, but leads one to think that UM16 is not contaminated near 1.0 m depth. The high Zn contents measured for horizons UM181 and UM182 are higher than the background content. These horizons are developed in the upper layers of a tertiary clay deposit (Landenian). The Zn content of this clay decreases abruptly from 2.0 m, below which it remains constant, indicating a contaminant accumulation between 1.5 m and around 2.0 m. This profile UM1 suggests the following hypothesis on the migration of this metal. The contaminant deposited in large quantities on the surface became partially soluble, due to low pH. Percolating with the soil water, it has been partially retained on the soil solid phase, down to a depth of around 0.8 m. Zinc remaining in solution was not readily retained by horizons UM16 and UM17, which are sandy and slightly acid to neutral. However, once the solution reached UM181, the clay slowed percolation, while the higher CEC and the pH neutral conditions favoured Zn retention. The Cd profile of UM1 had a similar aspect to that found for Zn and one may draw an identical hypothesis about the migration of Cd.

(2) The content of the earthworm galleries has, in most cases, higher Cd, Pb and Zn concentrations than those of corresponding horizons at the same depth (Table 1). This shows that the materials filling the galleries came, in part, from more contaminated horizons, situated above the sampling level. Most of the galleries were found at depths of less than one metre in contaminated horizons.

(3) The mobility of Pb was found to be similar to those of Zn, and much smaller than that of Cd. All the factors governing the mobility of Pb were not clearly distinguishable and seemed to be different from those affecting the movement of Cd and Zn. The depth reached by the metals increases with their concentration in the topsoil. Soil acidity and sand content facilitate the transfer of Cd and Zn. The mobility of Zn seemed to be favoured by organic matter in the topsoil. However, the concentration profiles are insufficient to evaluate the movement of the contaminants, as these can percolate without being retained by the solid phase of the soil. Moreover, the *in situ* approach and the statistical analysis used do not allow the contaminant flow to be quantified and mainly permit hypotheses to be drawn as to the transfer mechanisms.

Table 1. Total Cd, Pb and Zn in the different sampled horizons.

Horizon	Depth cm	Cd mg.kg^{-1}	Pb mg.kg^{-1}	Zn mg.kg^{-1}
M61+2	12	18.2	985.0	1390.0
M63	32	0.501	25.7	72.8
M64	47	0.245	20.9	64.2
M65	68	0.142	18.9	64.1
M66	96	0.102	18.3	53.6
M671	116	0.059	14.4	46.2
M672	139	0.063	11.3	39.8
M68	160	0.045	8.9	25.8
M811	2	43.0	3550.0	2035.0
M812	5	67.0	4890.0	2685.0
M82	9	10.1	225.0	671.0
M831	20	3.633	158.2	309.0
M832	36	1.362	58.9	115.0
M84	63	0.588	33.5	66.3
M851	95	0.307	20.0	51.8
M853	147	0.119	16.0	51.9
Earthworm galleries				
M84	63	3.383	103	299

Horizon	Depth cm	Cd mg.kg^{-1}	Pb mg.kg^{-1}	Zn mg.kg^{-1}
UM11	4	149.0	2995.0	19690.0
UM12	16	305.0	5410.0	31175.0
UM13	32	14.0	250.0	2333.0
UM14	46	3.500	24.0	972.0
UM15	71	1.130	21.7	527.0
UM16	101	0.138	12.5	63.0
UM17	127	0.077	10.5	56.0
UM181	155	0.713	20.6	160.0
UM182	185	0.592	21.4	118.0
UM41	3	169.0	2340.0	11995.0
UM42	8	120.0	4480.0	8285.0
UM431	16	15.5	383.0	1819.0
UM432	29	8.900	343.0	1449.0
UM44	44	4.300	21.7	767.0
UM45	59	2.650	18.2	612.0
UM46	79	0.241	17.1	157.0
UM471	107	0.179	12.4	66.0
UM472	136	0.059	11.6	49.0
UM48	155	0.112	10.2	36.0
UM911		0.556	38.3	82.0
UM912	16	0.377	38.6	99.5
UM92	35	0.218	21.4	64.8
UM93	64	0.114	15.8	47.1
UM941	91	0.152	20.6	62.4
UM95	144	0.065	12.8	35.2
UM96	174	0.141	15.6	44.5
UM97	197	0.144	16.6	52.2

Batch experiment

Soils sampling and analyses

The purpose of this part of the study was to evaluate the movement of metallic Cd, Zn and Pb through the unsaturated zone of a soil towards the aquifer, from the physico-chemical properties of the considered metallic cations and of the main soil constituents.

Six soil samples were chosen at different depths and were accurately characterised (acid-base titration, CEC, BET surfaces, chemical, mineralogical and granulometric composition, initial concentrations of Cd, Pb and Zn adsorbed). The distribution coefficients were measured using batch experiments. Influence of the total metal and Ca concentrations was studied at natural pH values.

Samples can be divided into 3 distinct groups :

(1) 1 sandy sample containing about 70 % of SiO_2 minerals,

(2) 3 clayey to loamy samples containing about 40-50 % quartz and calcite free,

(3) 2 calcite rich samples (about 10 %), poor in quartz (about 10 %).

CEC and BET surfaces increased from group 1 to group 3 due to differences of granulometry and mineralogical composition. The buffer capacity sequence is in agreement with the calcite content of the different soil horizons : group 3 >> 1 >> 2.

Results and discussion

Generally, the distribution coefficients decrease when the total metal concentration increases, which indicates classically a beginning of saturation of the adsorption sites of metal onto the solid. Because of the original concentration in metal in the studied samples and of the detection limit of the studied methods, we were obliged to use high metal concentrations in the batch experiments. We were thus unable to determine the true distribution coefficient (Kd) of the studied samples. Influence of Ca concentration on metal adsorption changed according to the different group of samples. An increase of Ca concentration did not influence adsorption onto the calcite rich samples (group 3) but strongly decreased adsorption onto the sandy sample (group 2). As Ca concentration increased, Pb adsorption onto the samples of group 2 decreased while Zn adsorption onto these samples did not vary a lot (adsorption of Cd was not studied for different Ca concentrations for these samples). These different behaviour can be explained by mineralogical differences among samples. Calcite rich samples lead to high Ca concentration in the aqueous phase so that the induced Ca variation within the experiment is negligible.

Metal adsorption sequences for the different sample group is : group 1 > 2 > 3. This sequence is the reverse sequence of the CEC and the BET surface one. This result indicates that cation exchange processes do not directly control sorption mechanisms. On calcite rich samples, the sorption can be related to metal coprecipitation processes leading to solid solution systems. On these samples, the observed sequence of metal adsorption Pb > Zn > Cd is in agreement with this sorption mechanism.

Soil solution concentration and role of colloids

Materials and methods

Zero-tension lysimeters were introduced at the lower limit of pedological horizons in UM4 (acidic pH) and M7 (alkaline, similar to M6). Soil solutions were collected after each major rainy period and filtered through a 5 µm diameter filter. Ultracentrifugation was performed in order to separate the colloidal and soluble fractions (Mavrocordatos & Perret, 1995). Total carbon, pH and trace metal elements contents were analysed, both in filtered bulk samples and in ultracentrifugated supernatants.

Results and discussion

Vertical transfer of Zn, Cd and Pb was shown, particularly in the surface horizon (Figure 3). The total metal element concentration in solutions decreased with depth. Soil solutions collected at the M7 site evidenced very low concentrations of Zn, Pb, and Cd (on average <100, <0.1, and 1-2 µg l^{-1} respectively). Soil solutions collected in the UM4 site are more concentrated, particularly for Zn and Cd . The high pH explained these differences. Pb concentration was in the same magnitude order in the both soils, as if the pH played a weak role in lead migration in these soils. In both soils, Cd concentrations in solution were higher than Pb concentrations, although the Pb content in soil is far higher than the Cd content.

In the acidic soil, colloidal species were responsible for less than 5% of Zn and Cd transfer in soils but about 30% of Pb transfer in the upper horizons (Figure 4). In the alkaline soil, solution Pb seemed to be soluble but a higher proportion of Zn or Cd (about 20%) was transfer-associated with colloids.

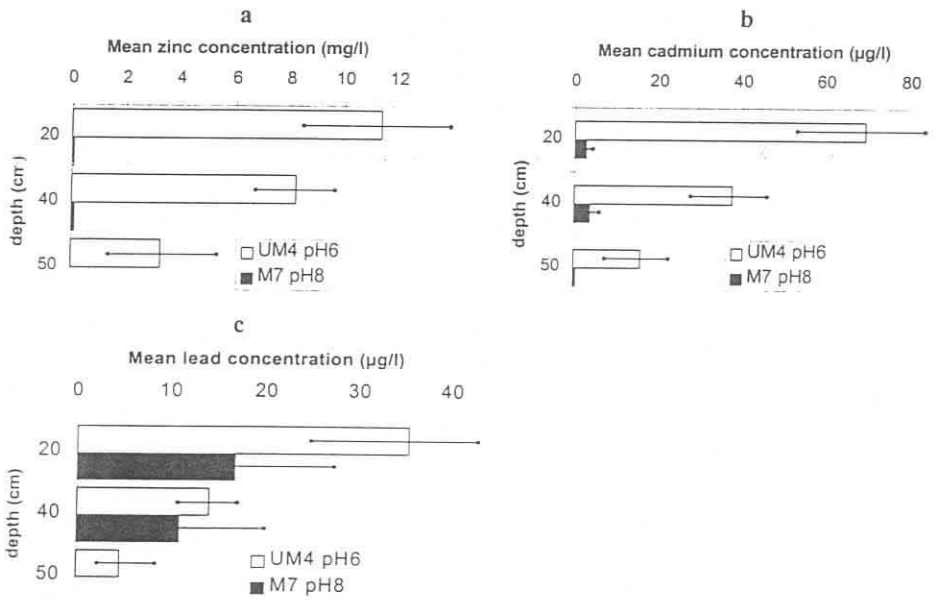

Figure 3. Average total concentration in the gravitational soil solutions collected in two polluted soils with different pH :

a : zinc,
b: cadmium,
c: lead

Different behaviour was observed during the year, depending on the soil moisture and the rainfall events (quantity and intensity). In moist periods, trace element contents and the proportion of colloids in the soil solutions decreased with increasing depth. On the contrary, after severe rewetting following a dry period a general increase of trace metal contents was observed with depth. In case of Pb, this increase was due to colloidal forms, which were released in the deeper horizon after a rapid rewetting of soil.

These results highlight rather high values of metal fluxes in metal contaminated soils. Zn and Cd transfer is important in acidic soils. An estimation of annual fluxes, in unsaturated conditions, indicates that about 2‰ of total Cd and Zn but only 0.03‰ of total Pb are transferred from the surface to 50 cm depth.

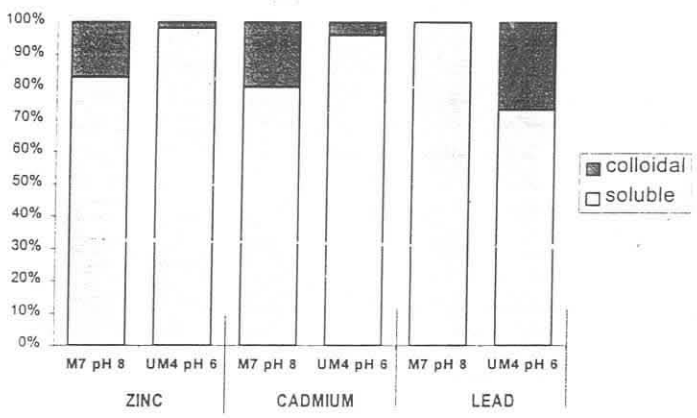

Figure 4. Average proportions of zinc, cadmium or lead associated with colloids or present in soluble form in soil solutions collected under the A-horizon in the both soils.

Porosity

Within the studied area, 4 profiles were submitted to a detailed investigation of soil porosity : M6, M7, UM8 (cultivated soils, with alkaline topsoil), M8 (grassland, acidic topsoil). All of them show amounts of at least one metal higher than 1000 mg kg^{-1}.

Sampling and methods

For the study of macroporosity, undisturbed samples of soil horizons have been taken at different depths and were then impregnated with resin. Thin sections (8 cm x 12 cm) were used to make 21 cm x 29.7 cm black and white photographs that have then been binarised for surface measurements. As the resolution of these images is 60 $\mu m.pixel^{-1}$, the pores observed are only macropores. The surfacic porosity is calculated by dividing the total surface occupied by pores by the investigated surface. The anisotropy parameter is given by the orientation of the major axis of the ellipse best fitting a considered pore, in comparison with a horizontal line in the image : pores are vertical if the angle is 90°.

To identify coarse mineral phases containing the contaminants and their location within the porosity, an undisturbed sample of the M8 surface soil horizon, the most contaminated, has been sampled perpendicular to the stratification. A thin section has been studied with an electron microprobe (Camebax SX50). Counting time for Pb, Zn and Cd was 20 s while it was 10 s for major elements as well as for P and S.

Results and discussion

The surfacic porosity varies from 10.4 % to 21.4 % (Table 2) and tends to decrease with depth as it is classically observed in soils. The macropore network is made of two sets : smaller pores (< 2 mm in diameter) represent more than 90 % of the total number of pores, while large pores (> 2 mm) are rare (about 50 in each thin section) but they account for 40 to 76 % of the total surfacic porosity (Table 2). As regards pore orientation, the four main directions

found on each thin section, horizontal (0°), vertical (90°), 45° and 135,° probably have a mechanical origin. Table 2 shows that the largest pores have a vertical preferential orientation that is particularly favourable for vertical transfers. This point will be investigated in a further 3D approach of the porosity.

Gommy (1997) and Sobanska (1999) indicate that metal-bearing particles are mostly found in the clay fraction. However, they also occur in the coarse fraction. In the M8, 8-16 thin section slags, glauconite grains and Fe- or Mn- hydroxyoxides appear to contain metals. They can be assembled into two groups : particles of anthropogenic origin and natural ones. Among these latter, some pre-exist the pollution (e.g. glauconite reworked from tertiary sands) while others are newly formed in the soil (some hydroxyoxides). The mechanisms of metal immobilisation could thus be different : either sorption in the case of pre-existing particles or coprecipitation in the case of the newly formed ones. In both cases, the metal-bearing particles are found in the immediate vicinity of pores indicating the great importance of the pore network in the fixation and transportation of the polluting metals, including the role of leached colloïds.

Table 2. Metric and anisotropy parameters obtained on the whole pore network and on the 50 largest pores in each thin section.

Profile, depth (cm)	Total porosity		50 largest pores	
	Surfacic porosity(%)	Number of pores	relative porosity (%)	preferential orientations(°)
M6, 14-22	20.4	3359	62	80
M6, 32-40	21.4	2548	76	90-100
M6, 70-78	12.7	2618	62	90
M7, 19-27	10.4	3005	40	110
M7, 47-55	20.8	3518	67	110-120
M8, 8-16	20.2	4057	62	50, 110
M8, 50-58	20.8	2858	71	90-100
UM8, 36-44	18.1	4787	39	110
UM8, 53-61	18.8	3958	58	80, 110
UM8 76-84	16.7	4468	53	50, 90
UM8 89-97	19.7	5365	45	50, 130

Conclusion

Despite a relative heterogeneity, the start of this programme was to focus different approaches of the same question on an unique site and even the same soils and samples.

Some traps, like the saturation of the adsorption capacity due to very high levels of pollutants, interactions between physical and chemical behaviour which can drastically change from one horizon to the following, the migration of coarse particles of initial dust or the neo-formation of insoluble compounds in the soil depth, may hardly complicate investigations or interpretations of observations. Moreover, as important features like the characteristics of porosity -including the role of earthworms- or climate events are not reducible to general laws, a naturalist approach based on a precise knowledge of pedological properties of soil seems to the most efficient way (if not the easiest) for risk assessment related to heavy metal transfer in contaminated areas.

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